Title: High -Performance/-Precision/-Z(HPPZ) Scintillator Grids via Advanced Electrochemistry Phase I – Project # 20210572MFR- Mid year review

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High -Performance/-Precision/-Z(HPPZ) Scintillator Grids via Advanced Electrochemistry

Phase I – Project # 20210572MFR- Mid year review

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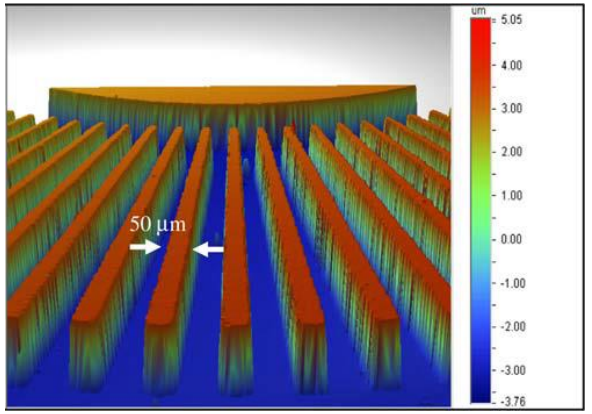
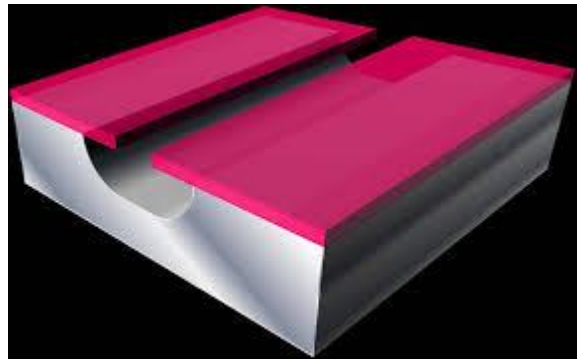
LAUR

Current Challenges/Needs

- Scintillation grids with improved imaging resolution in time and space, are required for future mission needs at various facilities (pRad user station, LANSCE, DARHT, Scorpius etc).
- Current technologies use inorganic crystal scintillators, which are positioned within a high-Z scintillator septa.
- Dense and high-Z materials are optimal for gamma-ray detection making them promising candidates for development of high -performance/-precision/-Z (HPPZ) scintillator grids.
- The current resolution of standard chemical etching and fabrication processes of high-Z materials is very low, leading to undesired undercutting and ultimately reducing crystal performance efficiency.



Optical profilometer 3-D image of 50 µm wide Ta electrodes patterned
J Mater Sci: Mater Electron (2007) 18:535–539



Undercutting during the wet etching process

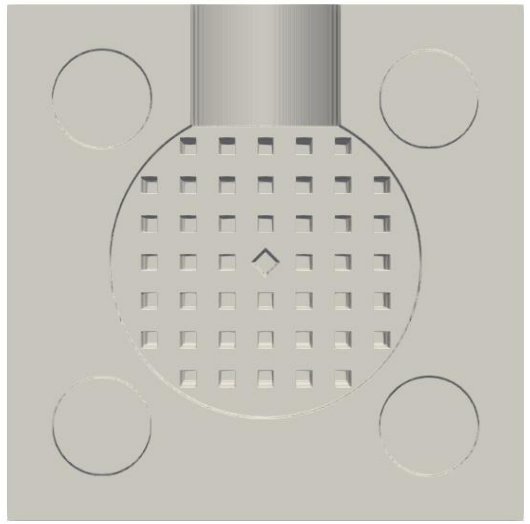
http://mocvd.ece.illinois.edu/research/presentations/MacEtch_2019_444%20lecture.pdf

Melcher C. L., "Perspectives on the future development of new scintillators." (2005), *Nuclear Instruments and Methods in Physics Research A,* **537**: 6-14.
Lowdon M., *et al.*, "Evaluation of Scintillator Detection Materials for Application within Airborne Environmental Radiation Monitoring." (2019), *Sensors*, **19**: 3828.
Moses W. W., "Current trends in scintillator detectors and materials." (2002), *Nuclear Instruments and Methods in Physics Research A*, **487**:123-128.

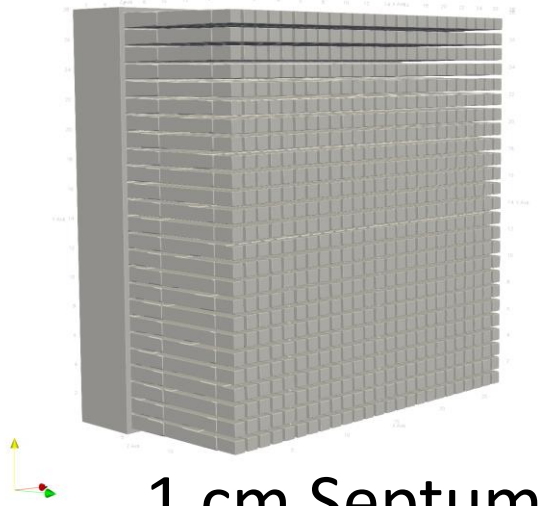
Target scintillator array design

- A high-Z material Bucky grid with specific dimensions is the required target by J-4 division.
- Tungsten (W), the currently used material for this metallic septa, is commercially etched into specific arrays via standard etching techniques.
- We propose the use of electrochemical deposition methods for large-scale scintillator grids with micron scale precision, from high-Z materials (Au or Re).
- Electroplating/electroforming is a mature metallic coating process, which involves deposition of metal over the desired substrate surfaces.
- Detailed electroplating/electroforming processes result in a homogenous, well-defined, conformal metal coating, which can be scaled-up for large scale applications at a low cost.

Small Grid Upstream



40-100 μm^2 columns



1 cm Septum

Giurlani W. *et al.*, "Electroplating for Decorative Applications: Recent Trends in Research and Development." (2018), *Coatings,* **8**:260. Hunt L.B., "The early history of gold plating." (1973), *Gold Bulletin*, **6**:16-27. Landolt D., "Electrodeposition science and technology in the last quarter of the twentieth century." (2002), *Journal of the Electrochemical Society*, **149**: S9-S20. Landolt D., "Electrochemical and materials science aspects of alloy deposition." (1994), *Electrochimica Acta*, **39**:1075-1090.

Goals

- Perform initial feasibility studies with the aim of producing complex parts for applications with difficult-to-process high-Z materials.

- Use of pulse and pulse-reverse electrochemical methods on additive approaches to produce high-precision Au and Re scintillator grids at a small scale.

- Follow up in Phase II with the delivery of a large-scale scintillator grid of the best material candidate with unprecedented properties for LANL needs determined in Phase I.

Project Plan

Activities	10/13/20	11/12/20	12/12/20	01/12/21	02/12/21	03/12/21	04/12/21	05/12/21	06/12/21
Task 1	Design/fabricate Au scintillation detector septa								
Task 1(a)	Thermal Diffusion Bonding								
Task 1(b)		Substrate removal via etching							
Task 1(c)		Collaboration with J4 team on septa array requirements							
Task 1(d)		Small scale proof of concept/Material characterization							
Task 1(e)				Large-scale electroplating process design					
Task 1(f)				Hot Isostatic Pressing process discussions for large-scale					

Project Plan cont.

Activities	10/13/20	11/12/20	12/12/20	01/12/21	02/12/21	03/12/21	04/12/21	05/12/21	06/12/21
Task 2	Electrochemical Deposition of Rhenium Films →								
Task 2(a)	Preliminary Electroplating →								
Task 2(b)		Pulse and pulse reverse deposition →							
Task 2(c)		Material/Film Characterization →							
Task 2(d)				Material feasibility for large-scale Re plating →					
Task 2(e)					Large-scale electroplating for a mandrel →				
Task 3									Report →

Gold-based scintillator arrays

- Au is a desirable scintillator material given its excellent malleability properties and its high-Z number.

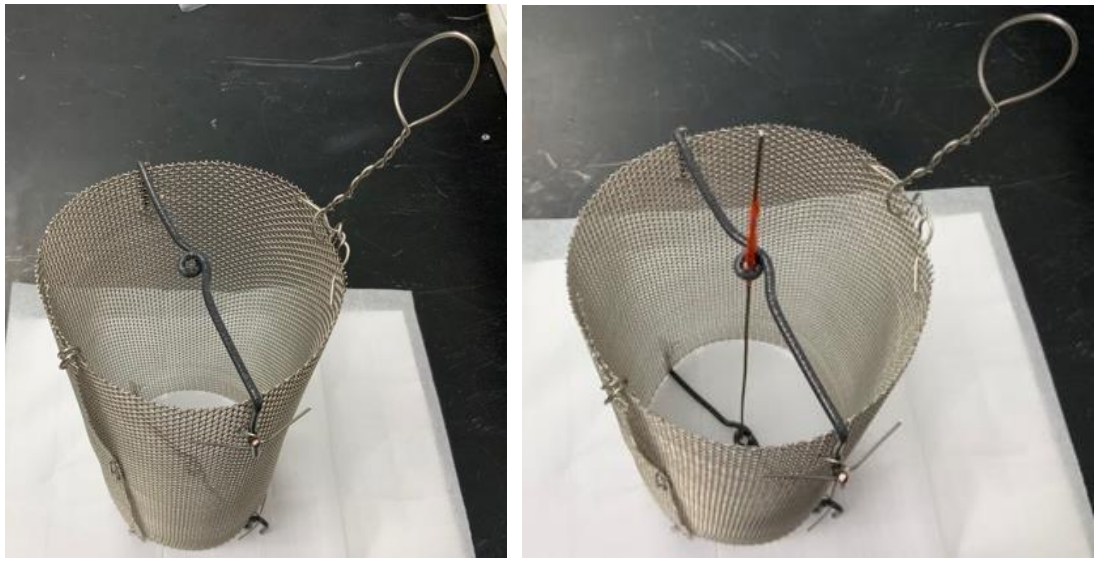
- Use of Au at this scale would normally be an unacceptable expense, however we currently have a stock of material with limited other uses that would be allowed for this application.

- Small scale: Proof of concept demonstration

  - Electrodeposition of Au on scintillator-geometry steel wires for thermal diffusion bonding and subsequent steel removal:
    - Electroplate steel square wires with the required dimensions
    - Bonding/fusing experiments
    - Dissolve the steel substrate leaving behind the Au scintillator grid

Experimental Details

- Steel square wires were machined at Sigma.
- A stainless steel mesh shaped into a hollow cylinder was used as the electrode.
- The wire was cleaned in a blue gold solution followed by an HCl bath (50 %) for 1 min.
- The wire was lastly dipped in an electroless Ni bath to activate the sample surface.



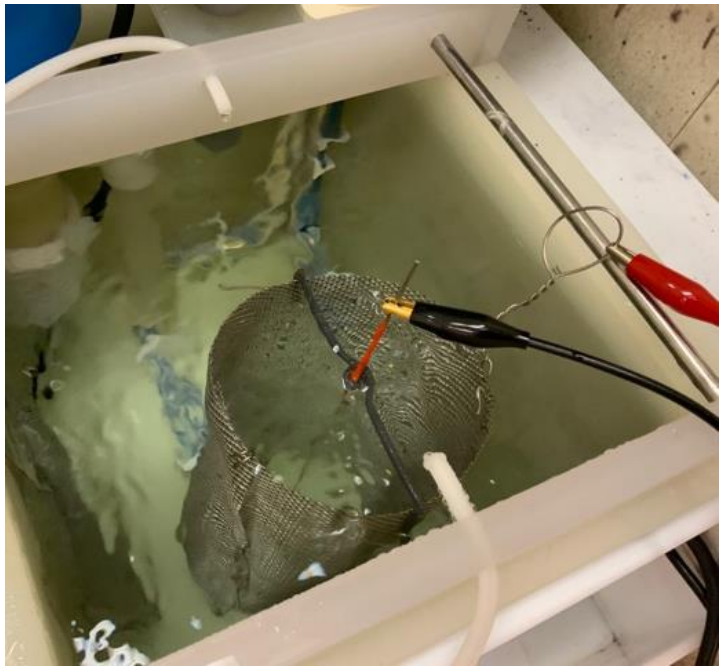
Stainless steel mesh electrode; Square wire positioned at the center using an insulated Cu wire.

Bare steel square wire

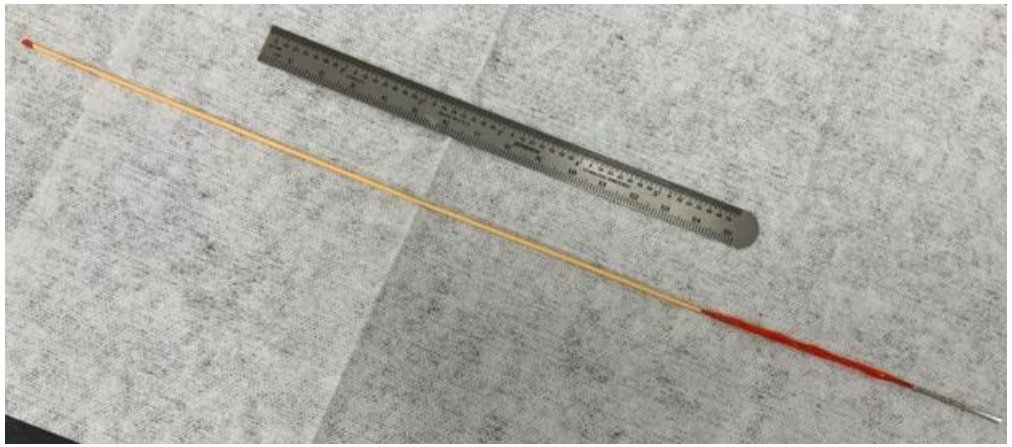
Paint was applied at both ends of the wire to mask the areas that will not be plated

Electroplating square wires

- Au electroplating solution was prepared using potassium gold cyanide and potassium hydroxide.
- Solution agitation through an appropriate pump is required to ensure dissolution of chemicals.
- The electroplating solution was heated to 60 °C and a standard current density of 0.02 A/in^2 was applied.
- To achieve a thickness of 0.004 inch, the wire was plated for ~8 hours.



Au electroplating set up

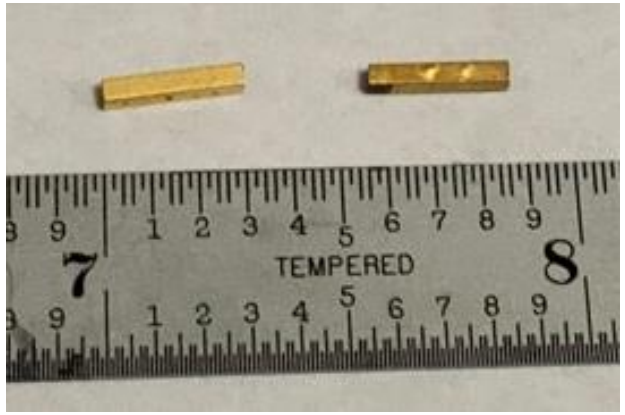


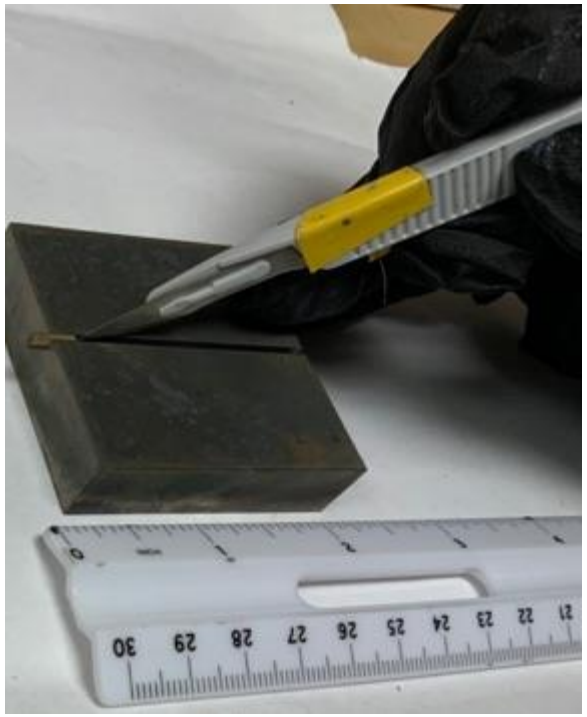
Au plated wire

Heat treatment/Bonding experiments

- The Au plated wire was cut into smaller pieces for bonding experiments and proof of concept.
- The Sigma machine shop manufactured a slotted block fixture to secure the Au-plated square wires during bonding.

The Au plated wire pieces





The slotted block fixture to hold the Au plated wire pieces

Heat treatment/Bonding experiments

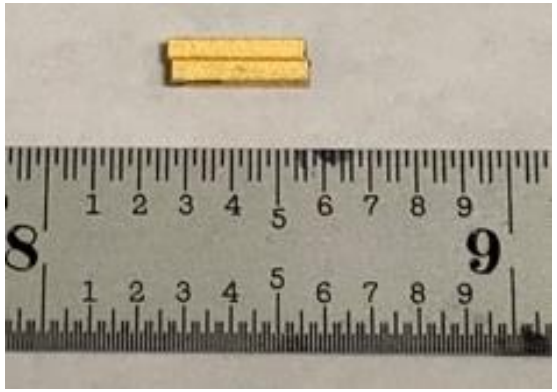
- A solid block was positioned on top along with 1 kg weight and the complete set-up was placed in the furnace.
- Heat treatment experiments were performed at various temperatures and times to optimize the bonding of the wire pieces.
- At lower temperatures the electroplated pieces (up to 550°C) bonded together, however they did come apart when using pliers.

Heat treatments using a furnace

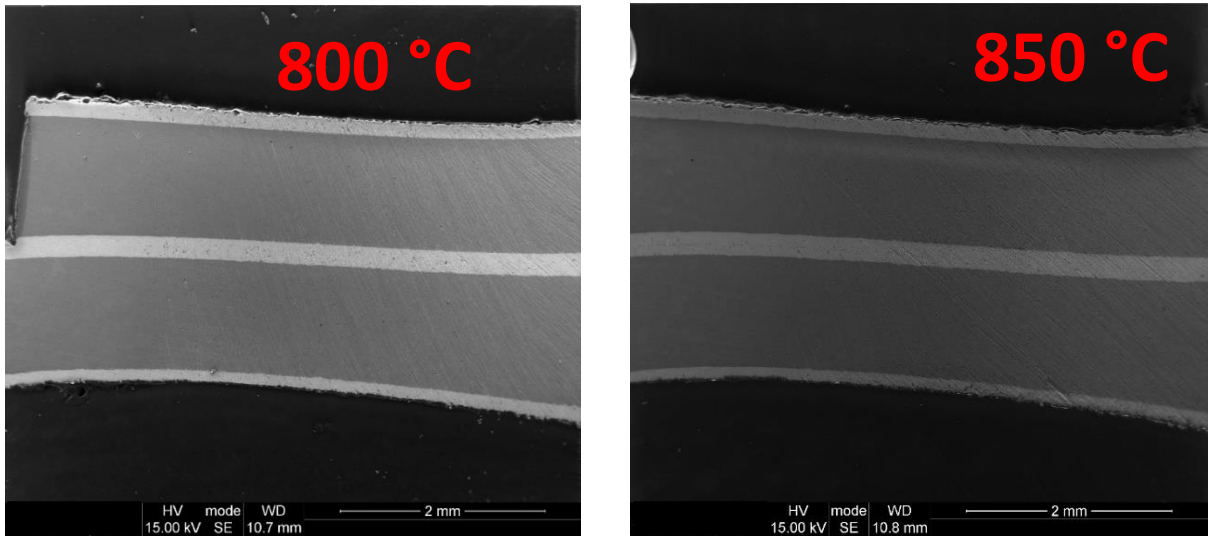
The Au plated wire pieces

Bonding experiments/characterization

- Heat treatments/bonding experiments were performed at 800 °C and 850 °C for 4 hours, respectively.
- To observe the interface between the wire pieces, the fused samples were cross-sectioned and prepared for SEM/EDS analysis.



Bonded Au plated wire pieces

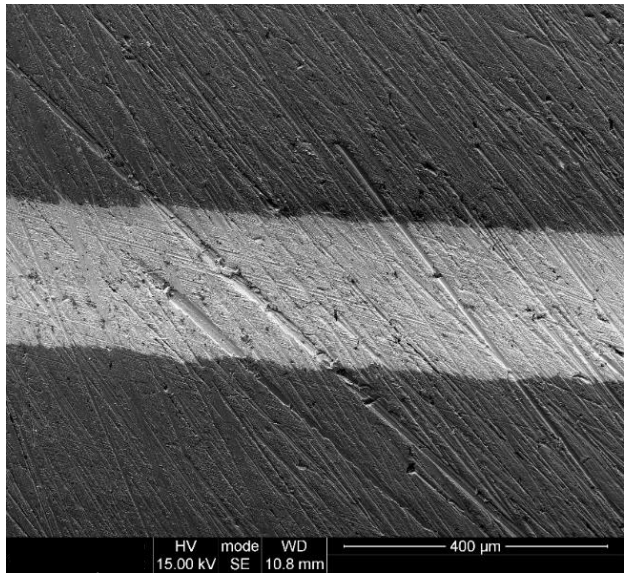


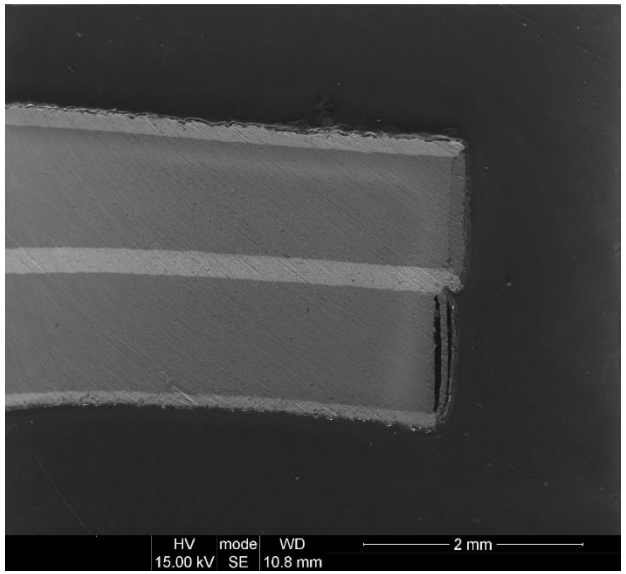
SEM images of the bonded wire pieces

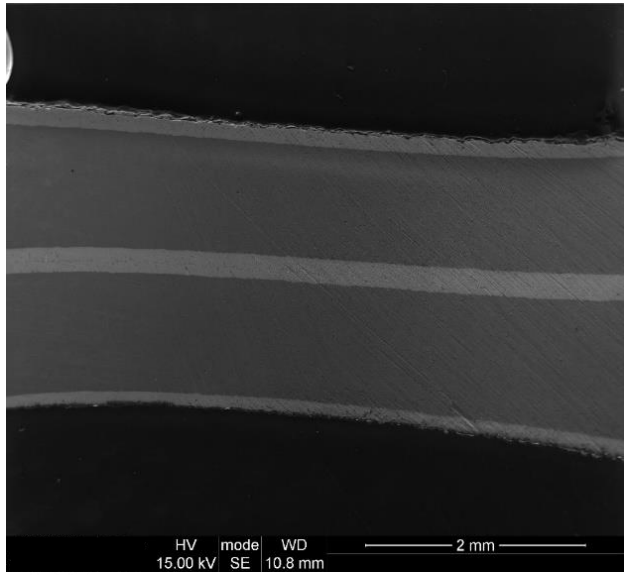
Bonded Au plated wire pieces after dissolving the steel substrate

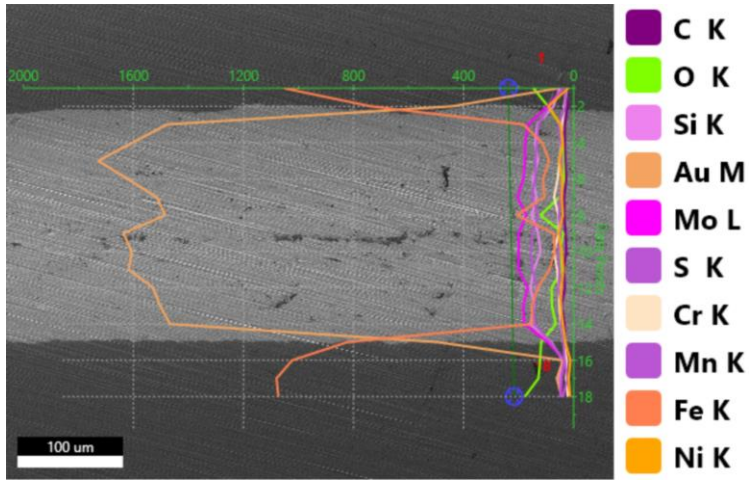
SEM/EDS cross-section analysis

Au square wires heated at 850 °C

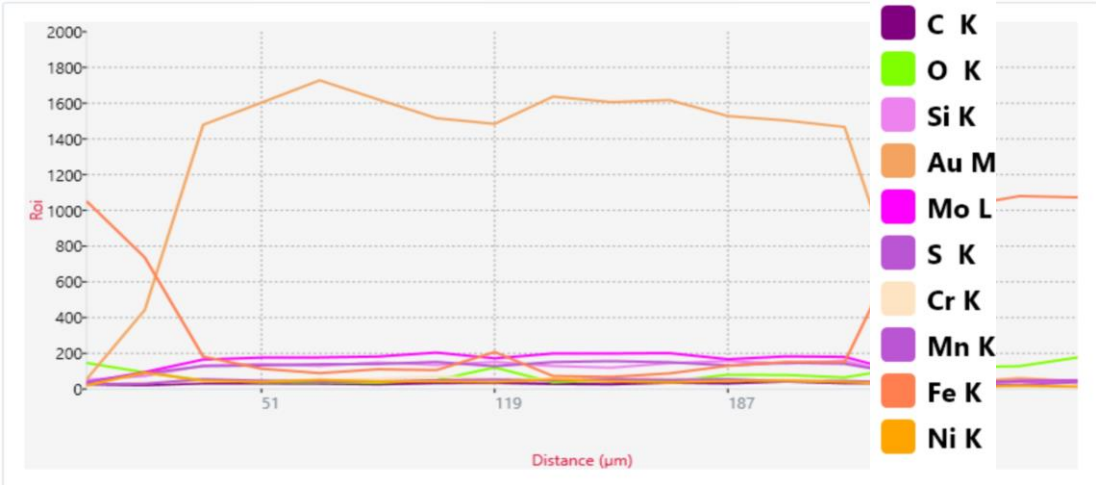






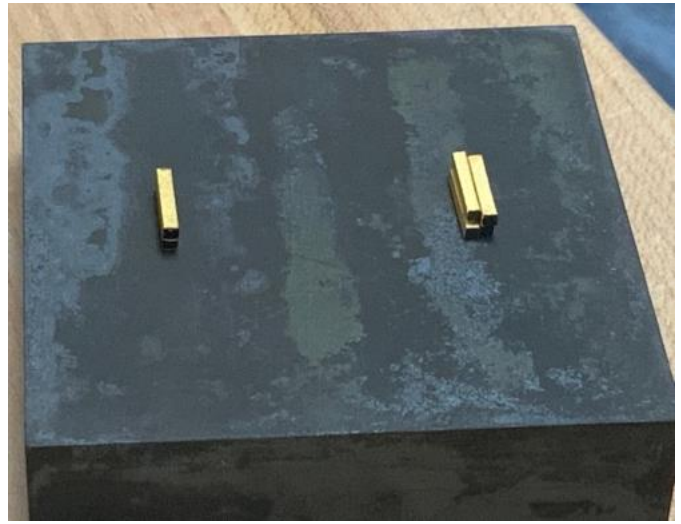


Element profile plot



Au array formation/design

- While all samples heated at 800 °C or 850 °C appeared fused, the ones at 850 °C were more mechanically stable.
- The rest of the structures were heated/bonded at 850 °C.
- The process was continued to develop a small-scale Au scintillator septa.



Stacked Au plated wire pieces after heat treatments

Stacked Au plated wires

Bonded Au plated wire pieces after dissolving the steel substrate

Large-scale Au plating process

- Design and set up large scale electroplating process of the square wires; *enabling plating of numerous parts at the same time*

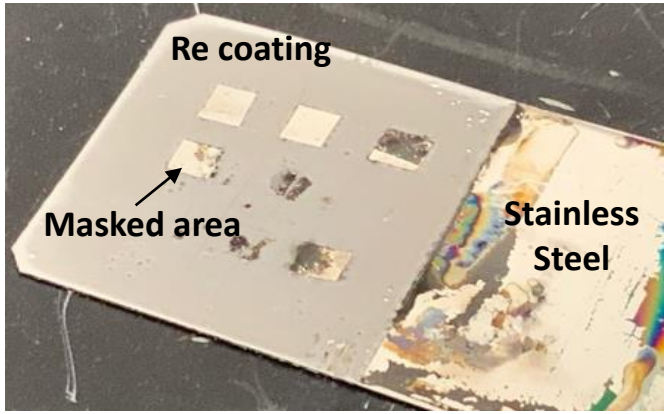
- Large-scale design
  - Purchase square wires with desired dimensions
  - Cut to the specific length
  - Large-scale barrel electroplating
  - HIP process development

Barrel plating baskets

https://singletoncorp.com/plating-mini-barrels-plating-baskets
https://www.platingbarrels.com/mini-plating-barrels

Rhenium Electroplating Pathway

- Re has a high-Z number and unique mechanical and chemical properties *(high melting point, high modulus of elasticity excellent wear and corrosion properties)*.
- Re can be electroplated and is significantly less costly than Au.
- However, deposits of pure Re are difficult to produce from aqueous solutions due to the low over potential for hydrogen evolution.
- Pulse electroplating allows for a finer control of metal deposition
- The goal is to electroplate thick Re films over a mandrel with specific grid patterns

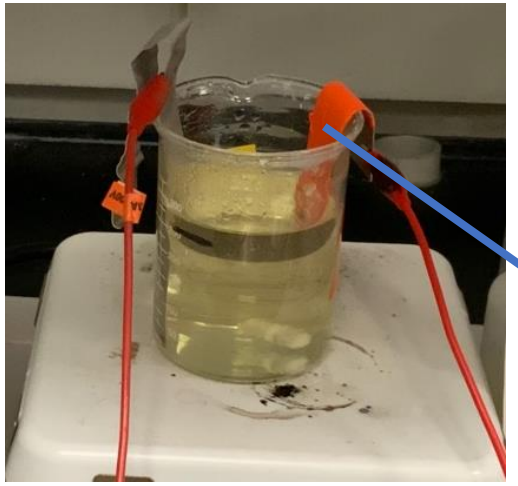


Re plated stainless steel substrate with masked areas demonstrating patterning feasibility.

Fink C. G. and Deren P., "Rhenium Plating." (1934), *Transactions of the Electrochemical Society*, **66**:471.
Camp E.K. and Watertown C., "Method and Bath for Electroplating Rhenium", Patented on Nov. 15, 1966, 3,285,839.
Tzippora Nusbaum *et al* 2015 *J. Electrochem. Soc.* **162** D250

Electrodeposition of Rhenium

- A stainless steel substrate was first dipped in a HCl bath followed by the deposition of a thin intermediate Ni film.
- The electroplating solution was composed of ammonium perrhenate (10 grams/liter), ammonium dihydrogen phosphate, (200 grams/liter) and ammonium hydroxide (28% by wt.).
- The solution pH was adjusted to 6 and heated up to 60 °C.
- Pulse electroplating with various on/off profiles was utilized for Re deposition



Stainless Steel substrate

Re coating deposition

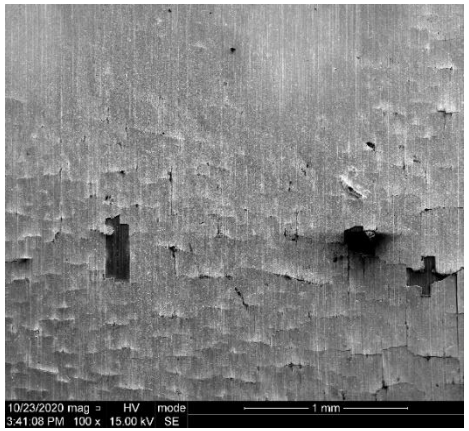
Pulse power supply

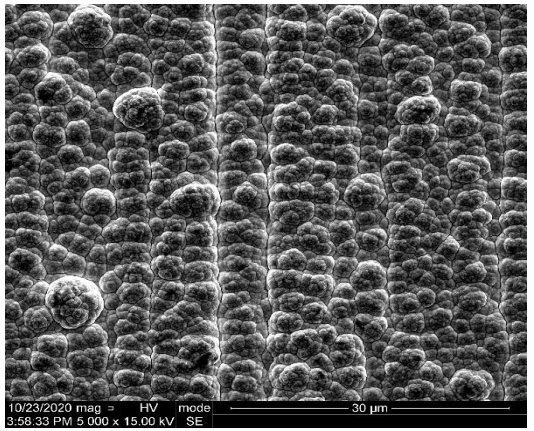
Ref: “METHOD AND BATH FOR ELECTROPLATING RHENUM”, by Eldridge K. Camp, Watertown, Conn., Patented Nov. 15, 1966, (3,285,839).

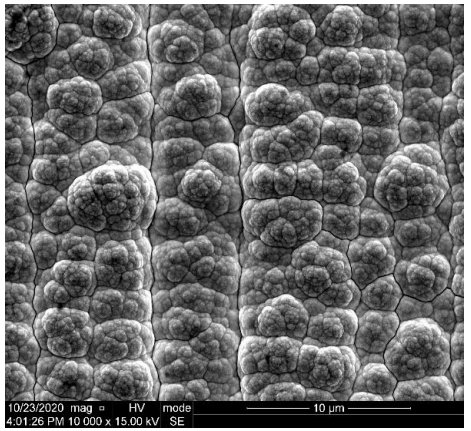
Investigation 1: Role of Substrate on Re Adhesion

Increasing Magnification

Stainless Steel







Parameters

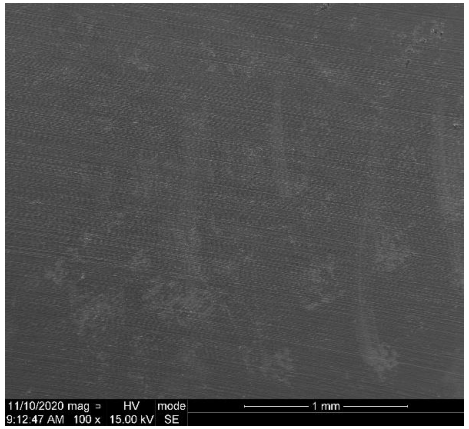
I_p= 3.5 A

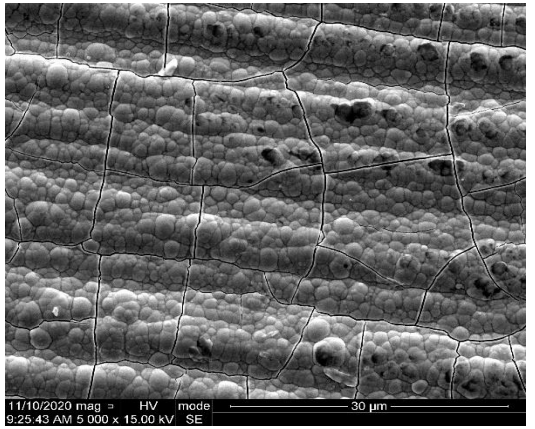
t_{on}=5 ms

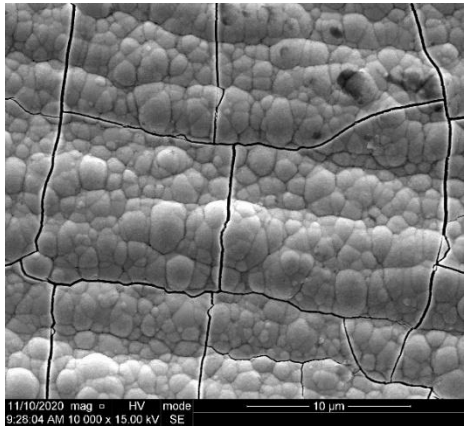
t_{off}=95 ms

T_{dep}= 4 hours

Stainless Steel + Ni



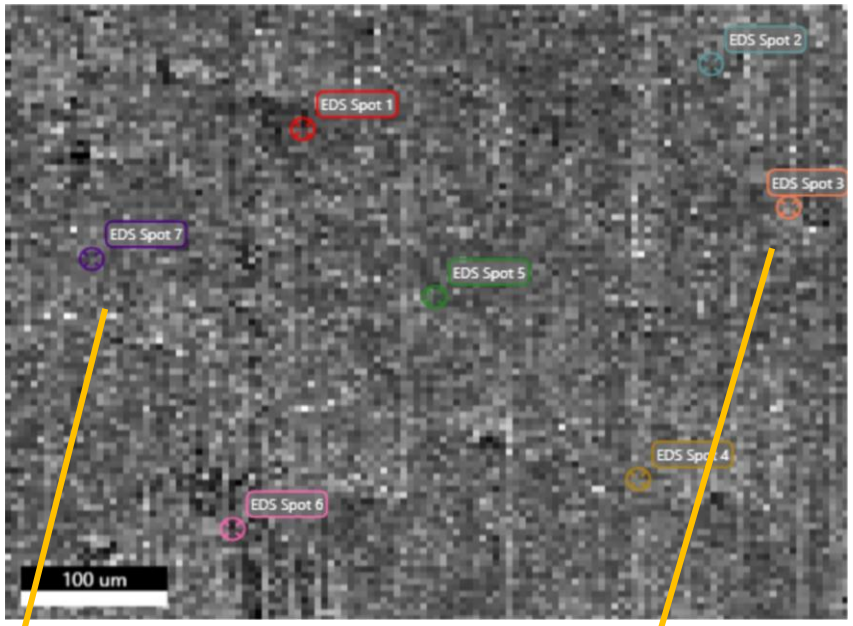


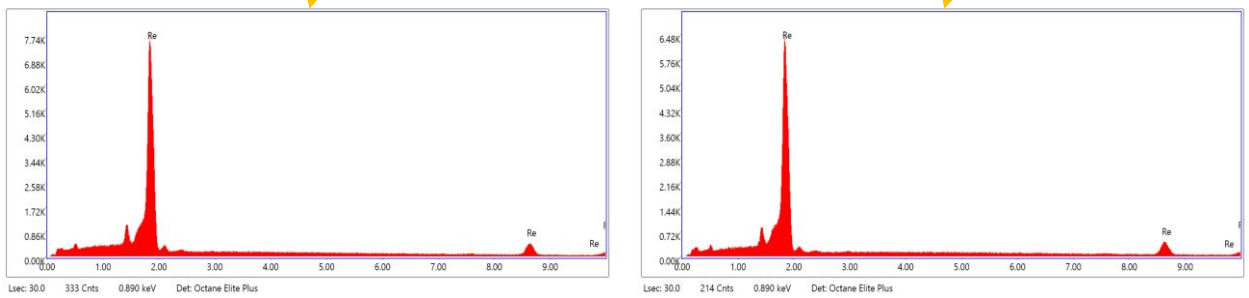


- Adhesion of Re on stainless steel is poor, resulting in macroscale cracks and a flaky film.
- A thin Ni layer improves adhesion, but micro cracks are observed due to hydrogen.

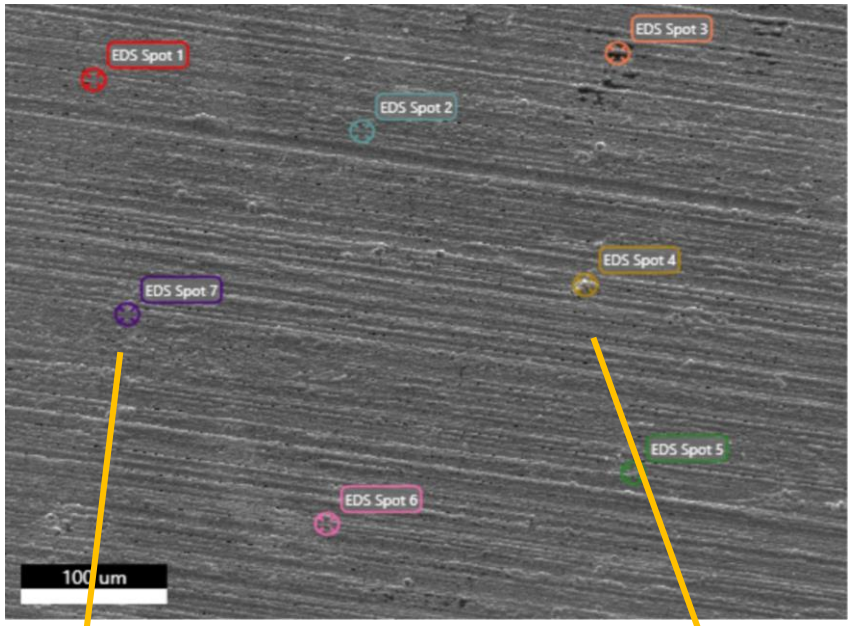
Investigation 1: Role of Substrate on Re Adhesion

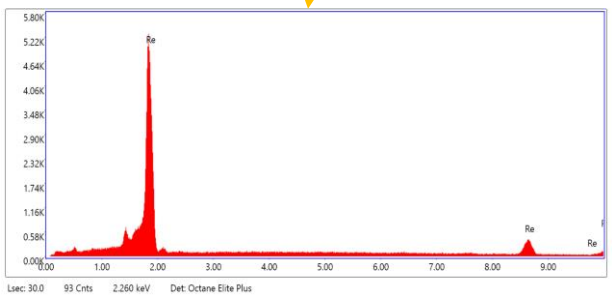
Stainless Steel

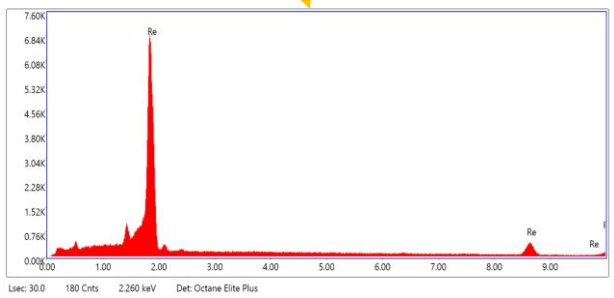




Stainless Steel + Ni



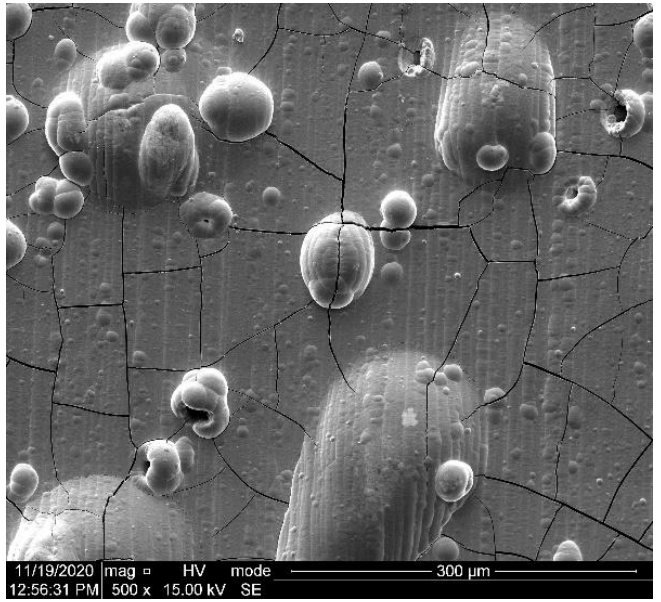


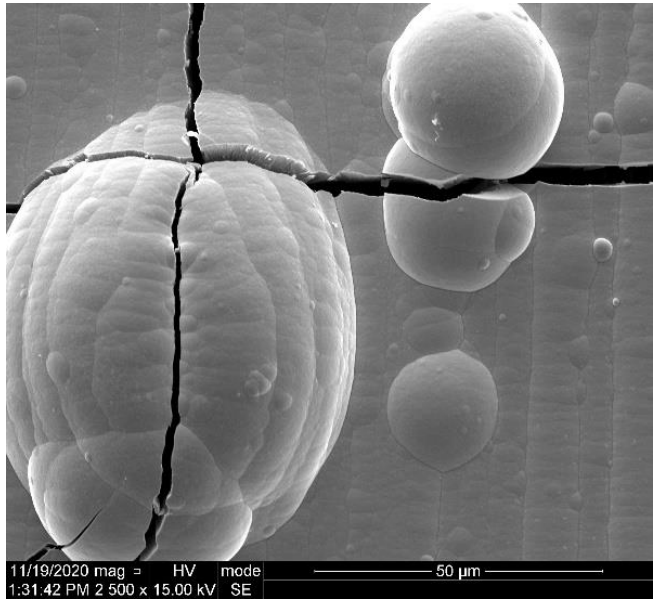


- Uniform, pure Re is electrodeposited on the surface

Investigation 2: Impact of Re Salt Chemistry

- Electroplating solution: $KReO_4$ (10 gr/l): H_2SO_4 (30ml/l)
- Hydrous magnesium sulfate was added to the solution until pH of 1 was achieved
- The electrodeposition was performed at 60 °C.
  - I_p=3.75 A
  - t_{on}=5 ms
  - t_{off}=95 ms
  - Deposition Time= 4 hours
- Large crack formation within the Re film was noticed after 4 hours of deposition



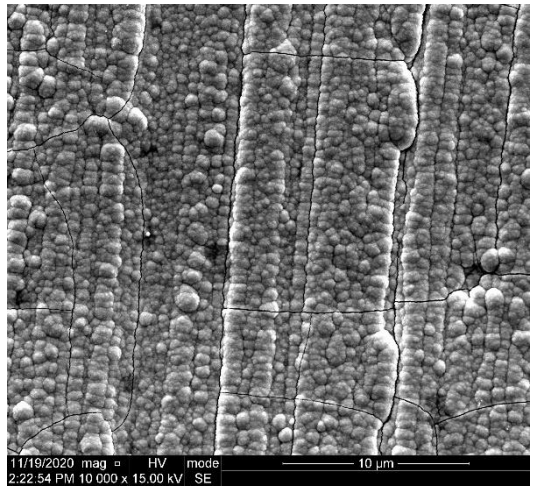


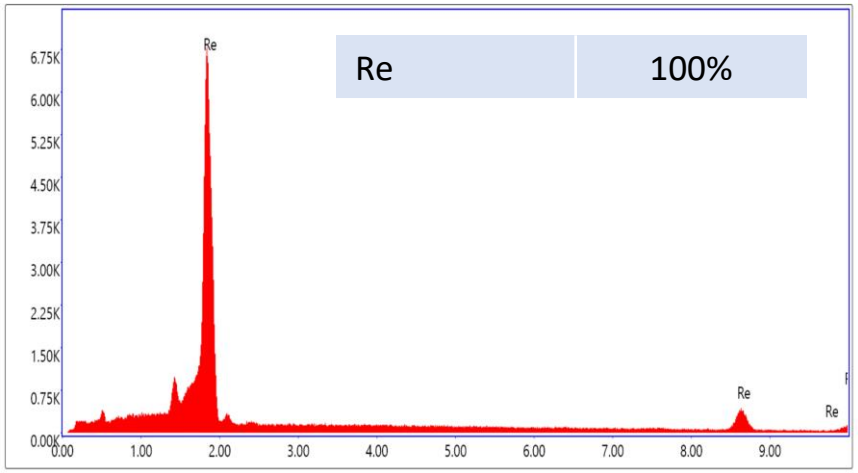
Colin G. Fink and P. Deren 1934 Trans. Electrochem. Soc.66 471

Investigation 3: Pulse vs Pulse Reverse Deposition

Forward Pulse

t_{fwd}5 ms Off Time 95 ms



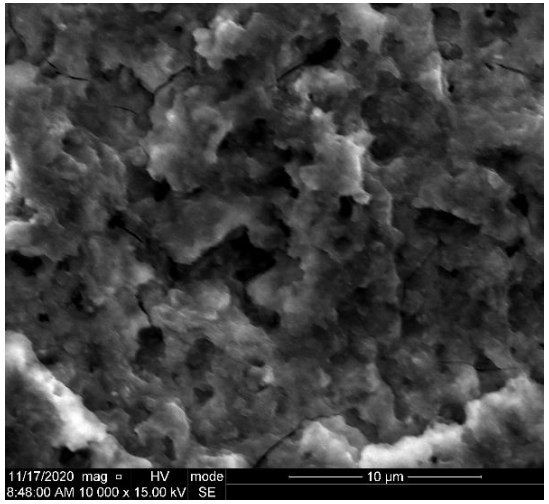


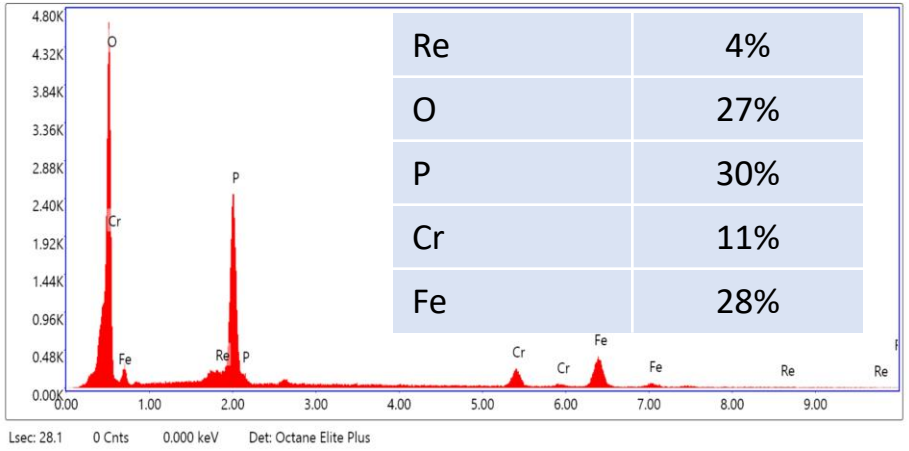
Re	100%

Pulse Reverse

t_{fwd}10 ms Off Time 87.5 ms

2.5 ms



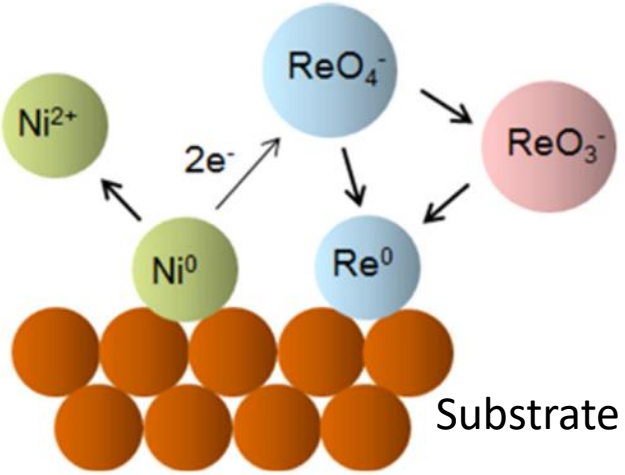


Re	4%
O	27%
P	30%
Cr	11%
Fe	28%

- Pulse reverse plating was investigated to aid removal of hydrogen generation.
- Initial pulse reverse parameters resulted in dissolution of cathode rather that Re deposition.

Co-deposition of Re-Ni Alloys

- Addition of metals such as Ni, Fe, Co to the electroplating solution increases the rate of Re deposition, while decreasing the hydrogen evolution rate and hence leading to significantly less brittle coatings.
- New Re-Ni electroplating solution for Re deposition at higher efficiencies with the aim of decreasing the micro-crack formation.
- Binary Re-alloy coatings posses higher oxidation resistance and thermal stability.
- Re-Ni films make excellent candidates for wear coating applications (replacing existing precious metals such as Rh which are more expensive) and in the aerospace industry.

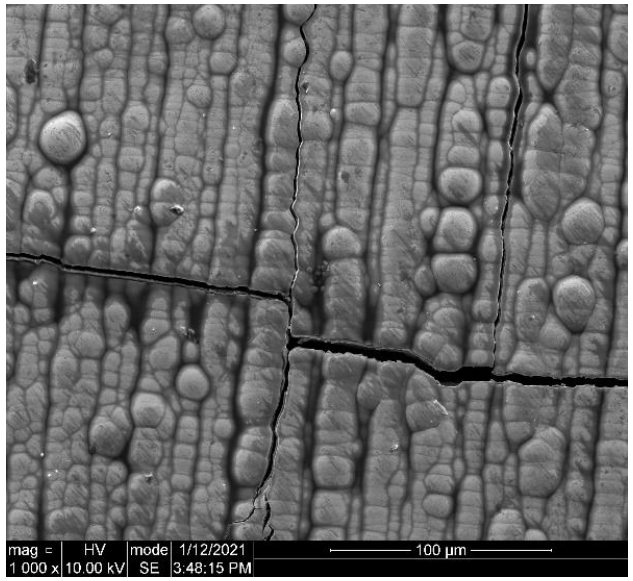


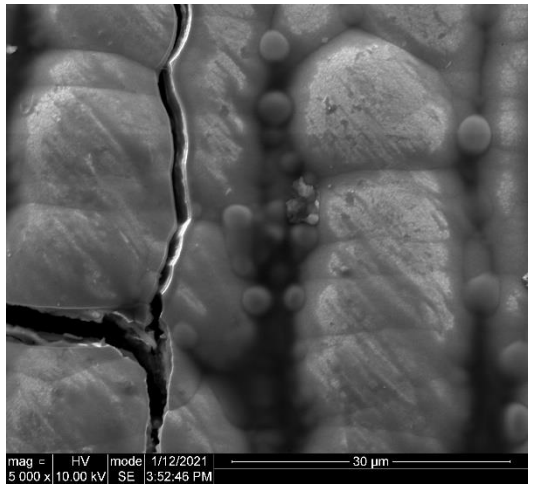
Schematic representation of the Re-Ni electrodeposition mechanism.
Baik et al, ADVANCED ENGINEERING MATERIALS 2016, 18, No. 7.

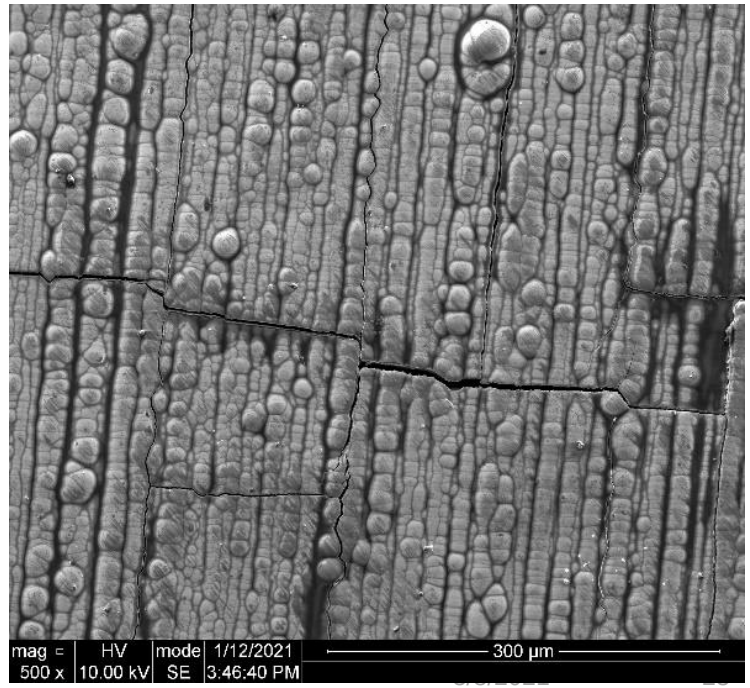
Tzippora Nusbaum *et al* 2015 *J. Electrochem. Soc.* **162** D250.
B. A. Rosen, E. Gileadi, and N. Eliaz, *Journal of Electroanalytical Chemistry*, **731,** 93 (2014).
Baik et al, ADVANCED ENGINEERING MATERIALS 2016, 18, No. 7.

Re/Ni Electroplating

- The Re/Ni electroplating solution was composed of ammonium perrhenate (50 mM), citiric acid (343 mM) and nickel sulfamate (93 mM)
- The solution pH was adjusted to 5 and heated up to 70 °C
- Pulse electroplating was carried out under these conditions
  - Area=0.25 in^2
  - I_p=3.5 A
  - t_{on}=5 ms
  - t_{off}=95 ms
  - Deposition Time= 2 hours
- A cracked but smooth Re film was noticed after 2 hours of deposition

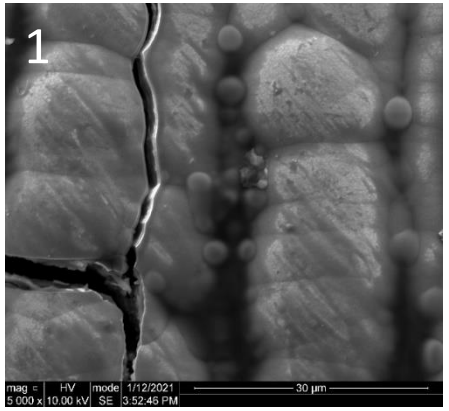


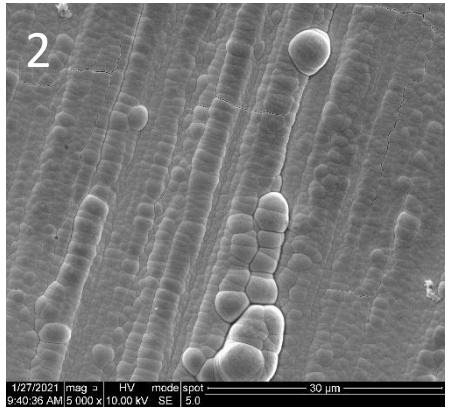


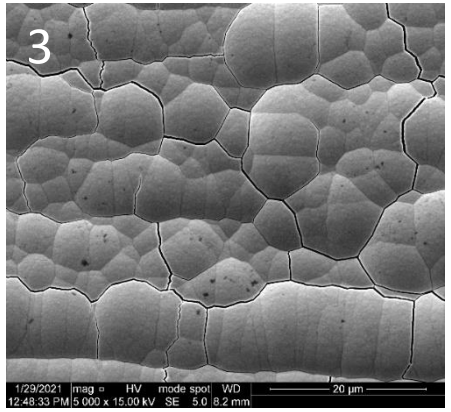


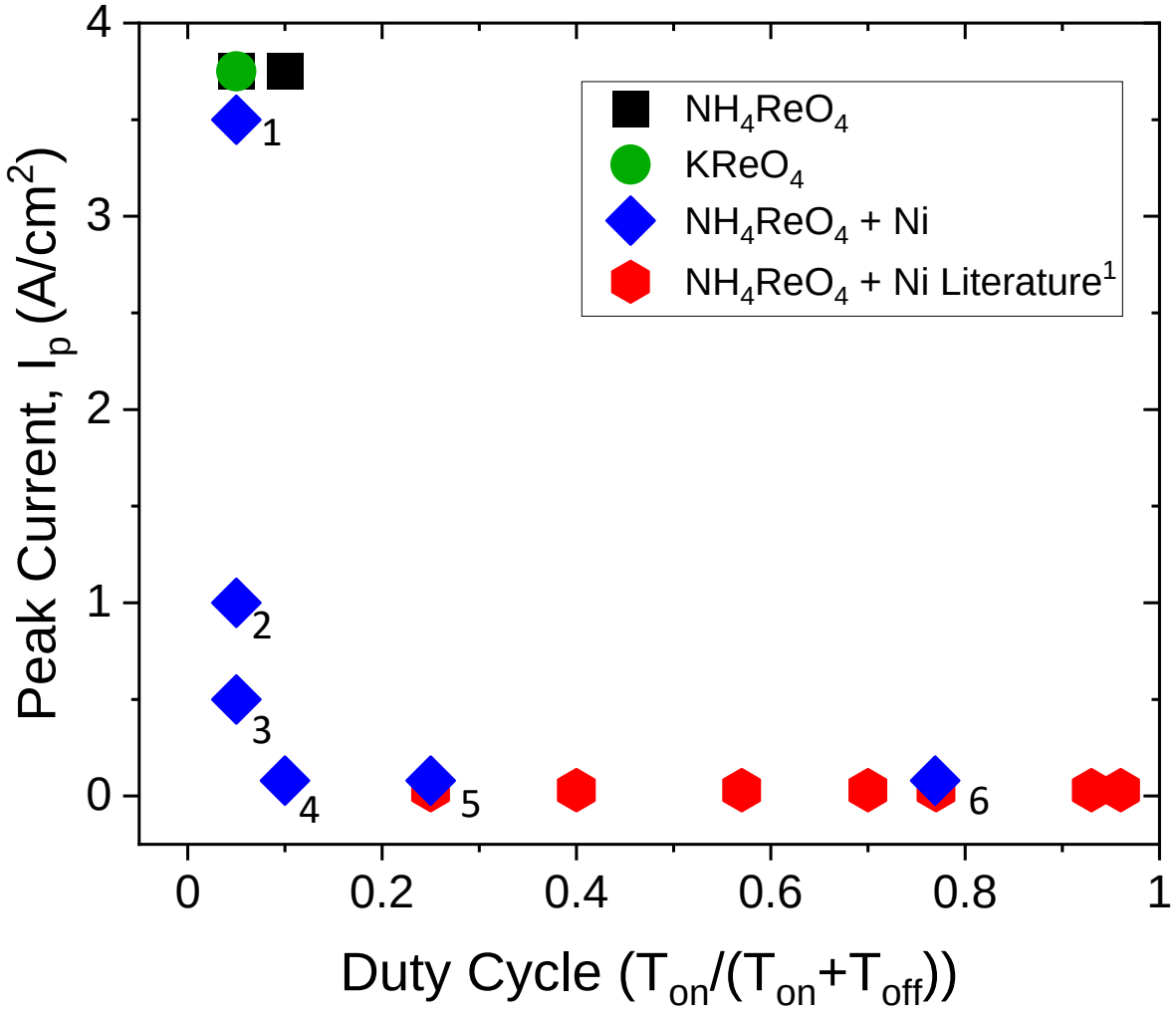
Tzippora Nusbaum *et al* 2015 *J. Electrochem. Soc.* **162** D250

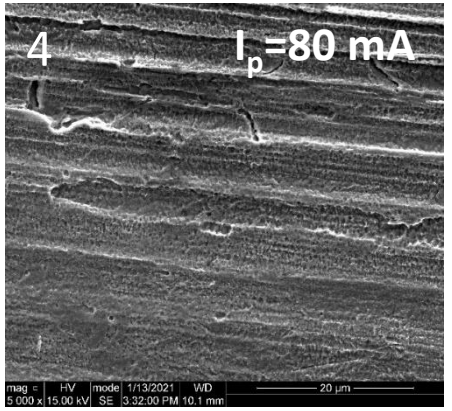
Re-Ni: Pulsed Electrodeposition Parametric Studies

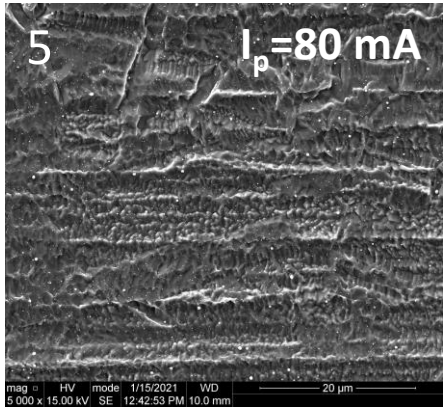


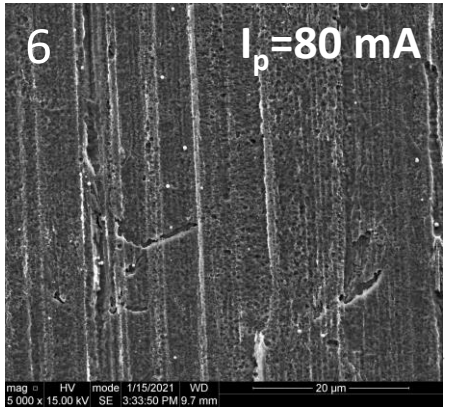








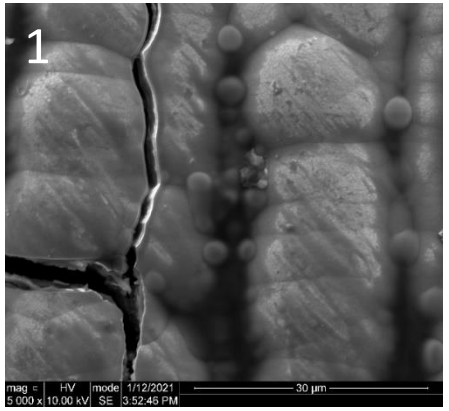


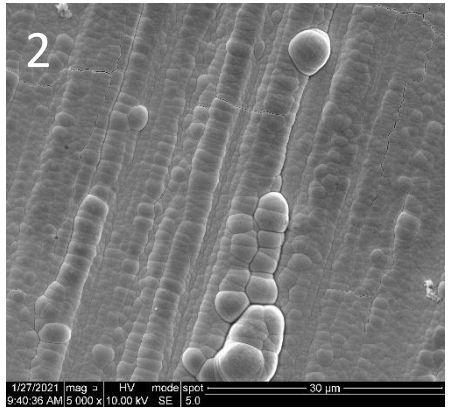


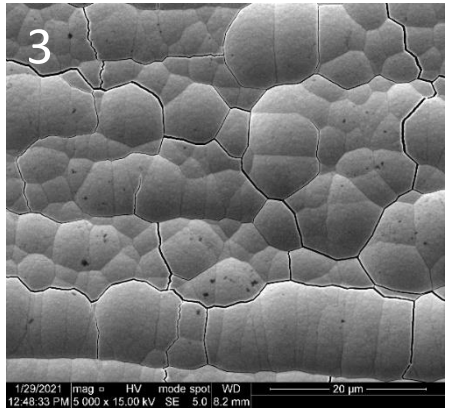
- Crack formation from hydrogen evolution can be reduced by reducing duty cycle and peak current, but at the expense of longer plating time

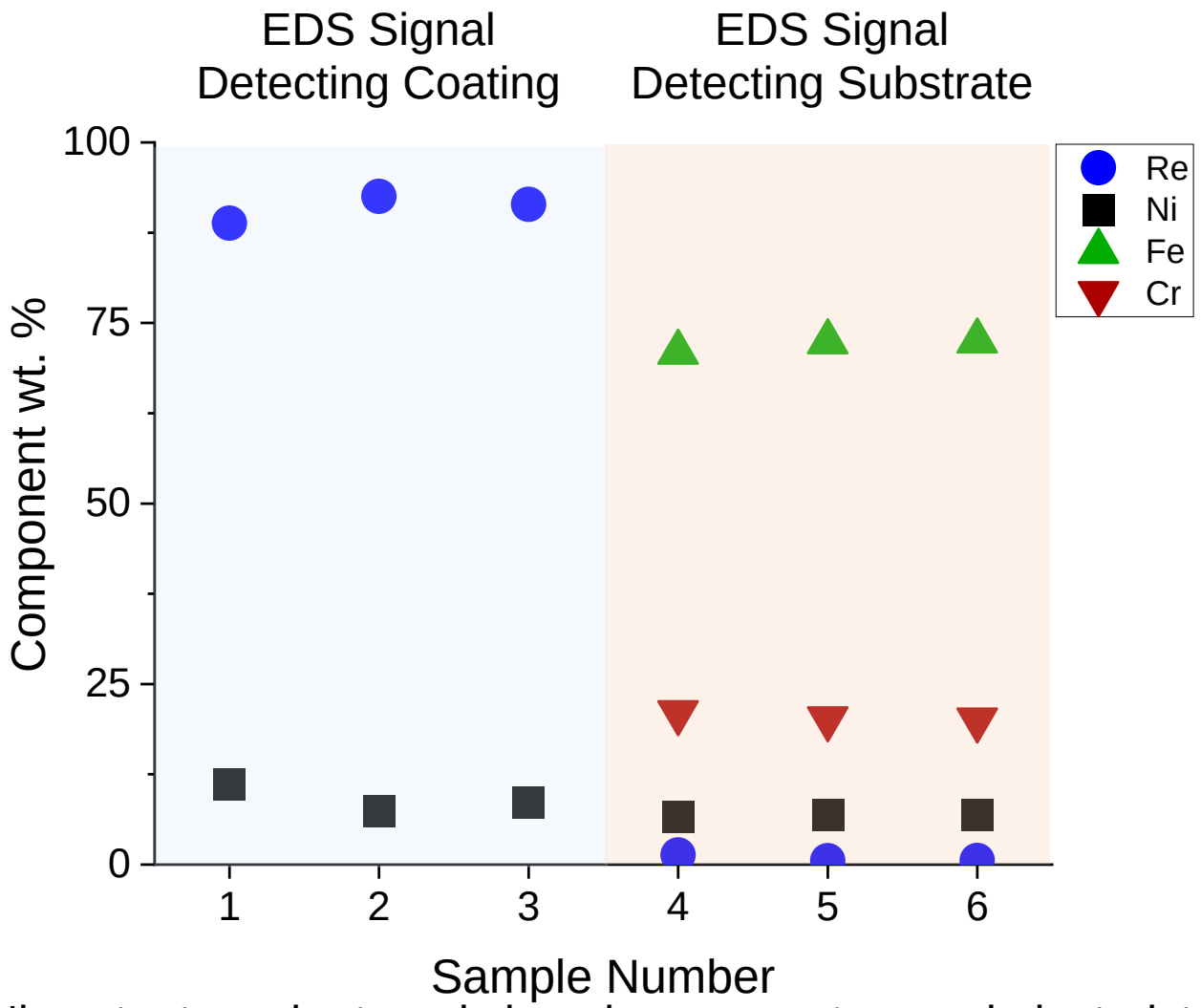
1] Tzippora Nusbaum *et al* 2015 *J. Electrochem. Soc.* **162** D250

Re-Ni: Pulsed Electrodeposition Parametric Studies

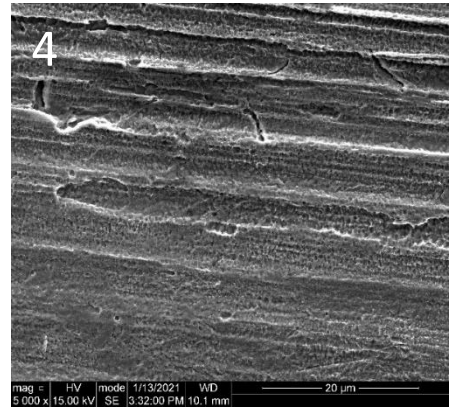


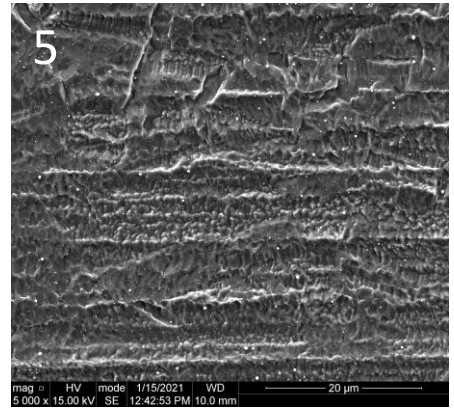


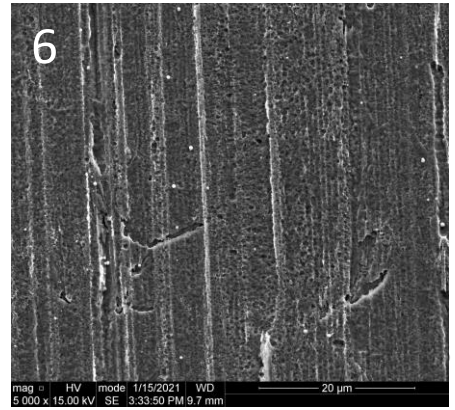




- Re/Ni content can be tuned via pulse parameters and electrolyte composition
- Re/Ni coating for samples 4-6 is too thin for EDS detection







Conclusions

- Initial small-scale feasibility studies to develop Au scintillator grids were successfully achieved.
- Re films were deposited via pulse electroplating methods.
- Transition in Phase II with the delivery of a large-scale Au scintillator grid meeting the J4-division target needs.

Au array grid

Progress/Future Plans

- Limited on-site presence due to COVID-19
  (November, December, January)
- The project is on track to meet objectives and enter the Phase I/Phase II down-selection
  - Follow up in Phase II with the delivery of a large-scale Au scintillator grid
- Plans for the next 3 months
  - Large-scale design for Au scintillator grids
    - Transition plan for Phase II
  - Re film development
    - Electrochemical studies on Re deposition
    - Wear studies on Re/Ni films

Project budget

Working with our CFO to stay on Target

Project Number	Project Name	Task Number	POC	Previous Month End Budget	Budget	Anticipated Budget	Planned Carryover	Available Budget	February Actual Costs	YTD Actual Cost	% Costed	YTD Balance Based on Budget	Burden Labor Forecast	Burden Non-Labor Forecast	Remaining Forecast	Projected YE Balance Based on Available Budget	Budget Less YTD Costs Less Remaining Forecasts
XXBB00	XXBB00: High -Performance	00000000	Dervishi	164,000	164,000	(25,000)	0	139,000	15,282	38,393	23.41%	125,607	36,549	875	108,414	(7,807)	17,193
XXBB00 Total				164,000	164,000	(25,000)	0	139,000	15,282	38,393	23.41%	125,607	36,549	875	108,414	(7,807)	17,193
Grand Total				164,000	164,000	(25,000)	0	139,000	15,282	38,393	23.41%	125,607	36,549	875	108,414	(7,807)	17,193

Code	Team Leader	Point of Con	Task	CC	Resource	Comment	Hours Forecasted	Burden Labor Forecast	Burdened Non-Labor Forecast	Sum of Burden
XXBB00	Hooks	Dervishi	00000000	3S020A	Clark, Courtney Logan	332002: Per Enke 2.18.21	110	16,991	0	16,991
					Dervishi-Whetham, Enkeleda	344558 FY21 Planning per Enka	185	0	0	36,984
					Edwards, Randall Lynn	344558 FY21 Planning per Enka	102	0	0	18,236
					Expected Funding	332002: Per Enke for Jacob Mendez2.18.21		0	0	
					Hooks, Daniel Edwin (Dan)	344558 FY21 Planning per Enka	51	0	0	15,769
					Materials	332002: Per Enke 2.18.21	0	0	875	875
					McBride, Michael Anthony	332002: Per staffing plan	110	19,558	0	19,558
				3S020A Total			557	36,549	875	108,414
			00000000 Total				557	36,549	875	108,414
XXBB00 Total							557	36,549	875	108,414
Grand Total							557	36,549	875	108,414

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Acknowledgments

- LDRD Office/MFR funding
- Sigma Management
- Courtney Clark for material characterization
- Samantha Lawrence for DC-ing the information

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Thank you!

Questions?